

## Some Aspects of Humidity Control in the Storage of Salt-Cured Calfskins

The inability of bacteria to grow rapidly on salted calfskins containing less than 48 per cent moisture<sup>1</sup> suggests the desirability of storage under conditions whereby the skins could be brought into equilibrium with the atmosphere and held at a moisture content of about 45 per cent. If this were possible salt-cured skins could be kept in storage without great danger of bacterial decomposition, while at the same time drying that would tend to promote irregularities and difficulties in soaking and tanning could be avoided.

An attempt was made to bring finely chopped, salt-cured calfskin into equilibrium with atmospheres of known relative humidities at a range in laboratory temperature of from 25° to 28° C., followed by determination of the moisture content. Composite samples were made from four salted calfskins in various stages of preservation. These were diced into pieces about one-quarter inch square after the hair had been clipped off and the excess salt removed from the flesh with a brush. Each sample was thoroughly mixed and a portion was removed for the determination of moisture and salt content.

Moisture was determined by drying in an electric oven at 60° C. for 48 hours. Salt was determined by digestion of the dried skin with hot concentrated nitric acid containing an excess of standard silver nitrate solution

followed by titration with 0.1*N* sodium sulfocyanate in the presence of a ferric indicator.

The remaining portion of each sample was divided into two equal parts. One part, representing green-salted skin, was immediately transferred to a glass jar which was sealed and temporarily stored at 45° F. The other half of the sample was spread out on an enamel tray and air dried in the laboratory for four days to represent dried, salted skin. It was then sampled for moisture.

Weighed portions of the prepared samples were conditioned according to the method recommended by Wilson<sup>2</sup>. The relative humidity of the en-

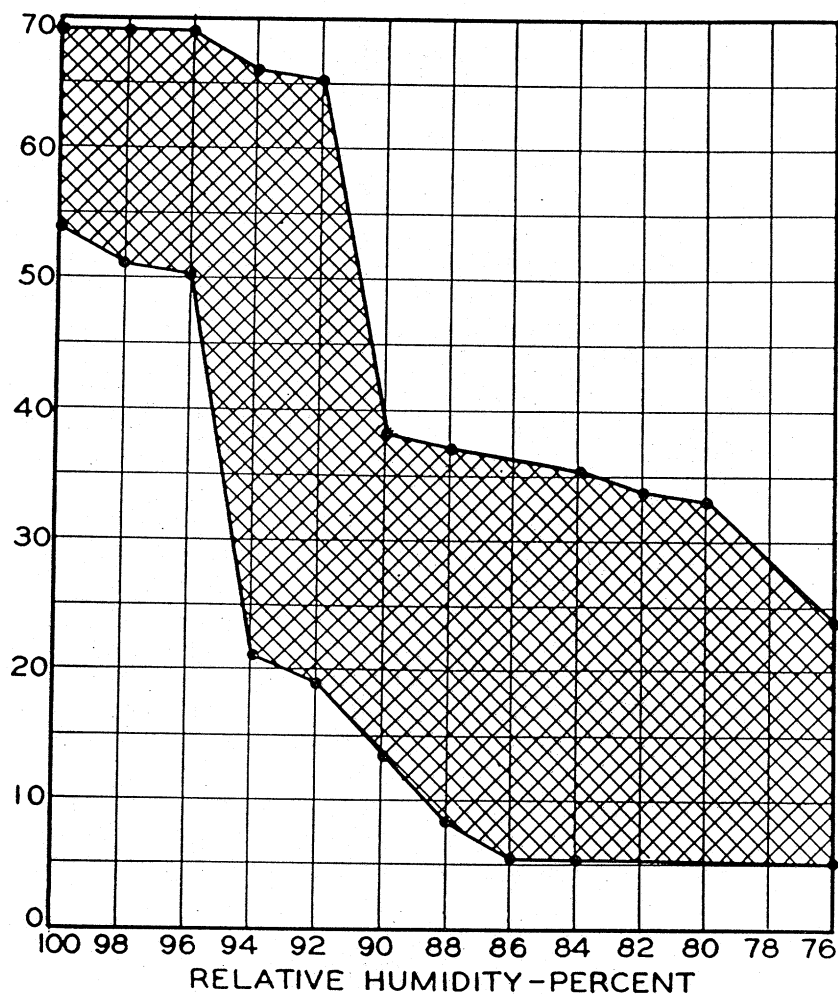


FIGURE I. Approximate weight equilibria of salt-cured calfskins at different relative humidities.

trained air was controlled by sulfuric acid solutions of the percentage composition given on Wilson's chart. A train of three bottles was employed, followed by filtration of the air through glass wool. The first bottle in the train was refilled every twenty-four hours with fresh sulfuric acid solution. The rate of air flow was rather rapid, being practically two liters per minute. When approximate equilibrium was reached, moisture in the conditioned sample was determined.

It cannot be claimed that any of the samples, with the possible exception of the dried salted ones, maintained at the lowest relative humidities, ever came to actual equilibrium. At those humidities at which the skin tended to take up moisture rapidly it continued to do so indefinitely with the condensation of free moisture. For practical purposes, therefore, weights were taken as soon after the appearance of water of condensation as was possible.

With the dried salt-cured skin at relative humidities of 92 per cent or below, the uptake of moisture was very slow and approximate equilibrium was not difficult to attain. With green-salted skin at relative humidities of 90 per cent or less, the loss of moisture was very rapid at first but the rate slowed down with time. After conditioning for a week these samples continued to lose weight slowly but regularly. Thus, all of the values given for green-salted skin at these relative humidities may average slightly too high. Some of the results of these experiments are shown in Figure I.

The top curve in Figure I shows the maximum values that were obtained with green-salted calfskin. The bottom curve shows the minimum values gotten with dried salt-cured skins. Many results were obtained with other samples of both green-salted and dry-salted skins that fell within the zone between the two curves. For any given sample, duplicate results in fairly good agreement were obtained. Wide deviations were gotten in results from different skins, although the relative values for different humidities were about the same. These deviations have been attributed tentatively at least to differences in the composition of the salt with which the skins were cured originally and in the state of preservation. The values given that are greater than 65 per cent moisture for green-salted skin at relative humidities of 92 per cent and above are admittedly too high, as the samples were dripping wet when weighed.

The results in Figure I show a very narrow, critical relationship between relative humidity and the moisture content of salted calfskin. Between the limits of from only 90 to 92 per cent relative humidity, the moisture content of green-salted skin varied from 38.8 to 65.3 per cent. At from 94 to 96 per cent relative humidity, the moisture content of dried salted skin ranged from 22.2 per cent to 51.3 per cent. Thus variations in the moisture content of salted skin of from 26.5 to 29.1 per cent on the basis of the cured weight are shown to occur with differences of only 2 and 4 per cent in the relative humidity of the storage atmosphere. It would appear, therefore, extremely

difficult to maintain through humidity control a moisture content of from 40 to 50 per cent in salt-cured skins. It seems probable that a knowledge gained from practical experience of such wide variations in moisture content with slight changes in relative humidity had much to do with the development of methods for packing and handling now used in commerce for the curing, shipment and storage of salt-cured hides. Such methods reduce the area of exposed skin and take full advantage of the insulation value of the skin for maintaining the moisture content of the unexposed part within the pack or the bundle.

Skins may be bundled with either the flesh or the hair side out. It was deemed, therefore, of interest to determine moisture changes depending upon the side that is exposed. For studying the rate of loss of moisture at 60 per cent relative humidity and 30° C., a salt-cured calfskin was taken from a pack that had been down in cure for 30 days. The hair was removed with electric clippers. Circular disks were cut from the "bend" portion of the skin, using the lower half of a standard petri dish<sup>3</sup> as a pattern. Twelve disks were cut. Portions of the skin that remained were diced into pieces

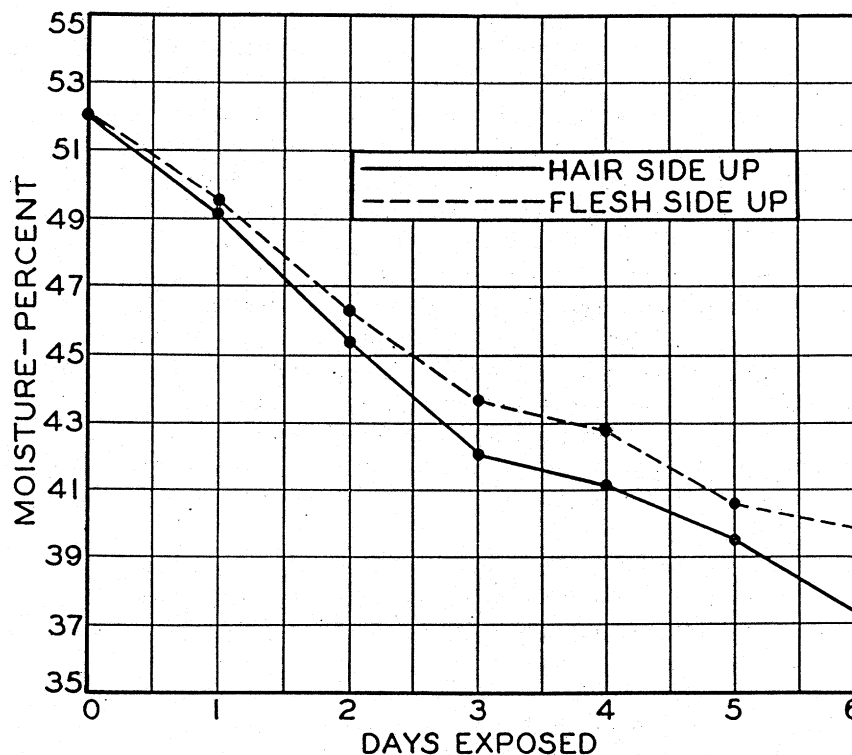


FIGURE II. Decrease in moisture content of salt-cured calfskin, exposed hair and flesh sides, respectively, at 60 per cent relative humidity and 30° C.

about one-quarter inch square and mixed as a composite sample for determining initial moisture and salt content. After weighing, each disk of skin was immediately fitted into the bottom part of a standard petri dish. Six disks were placed grain side up and an equal number flesh side up. The very narrow space between the edge of the disk and the wall of the dish was filled in each case with melted paraffin. This was done to reduce to a minimum the edge effect of the disk. The container and sample were then weighed and placed in a humid chamber on an elevated glass platform over a sulfuric acid solution adjusted to the desired concentration according to Wilson's chart. All humid chambers were stored in an incubator at 30° C. Each container with its sample was removed from the humid chambers and weighed daily for a period of six days. The daily opening of the small chamber undoubtedly introduced an error. The results, therefore, should be interpreted as comparative rather than as absolute values.

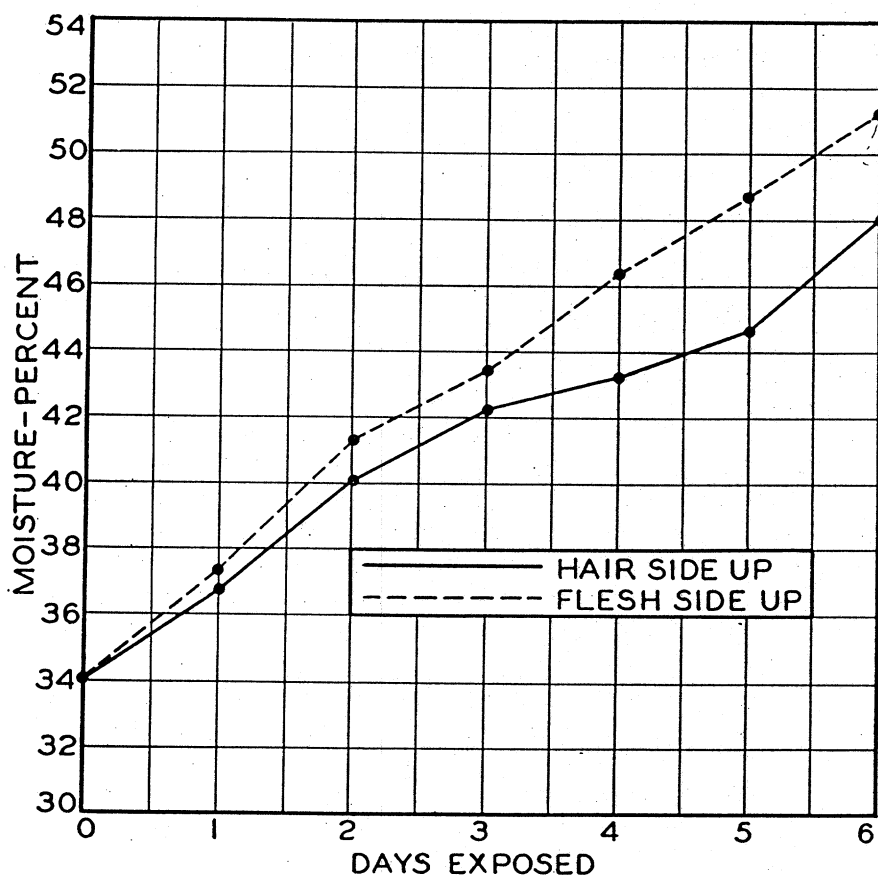


FIGURE III. Increase in moisture content of partially dried salt-cured calfskin, exposed hair and flesh sides, respectively, over water at 30° C.

The clipped, cured skin had an initial content of 52.1 per cent moisture and 12.7 per cent sodium chloride. The average moisture content of the 6 disks stored grain side up and flesh side up, respectively, at daily intervals during the storage period are shown in Figure II. The values are expressed on the basis of the clipped, cured skin.

From Figure II it will be seen that the moisture content of salted skin stored at 60 per cent relative humidity and 30° C. decreases rapidly. The rate of loss is slightly greater from the hair side. This might be expected since animal skin is so fabricated that the capillaries decrease in size from the flesh side outward, thus tending to make the moisture in the skin move toward the hair side through capillary attraction.

For studying the comparative rate of uptake over water, a salt-cured calfskin was allowed to dry in the laboratory to a state of partial dehydration. The skin was clipped and diced as previously described. The moisture content after partial drying of the skin was 34 per cent. Its salt content was 19.3 per cent. The average moisture content of 6 disks stored hair side up and flesh side up, respectively, for daily intervals during the storage period over water at 30° C. is shown in Figure III. The values are expressed on the basis of the clipped, cured skin.

The increase in moisture content of partially dried, salted skin stored over water takes place rapidly from both the grain and flesh sides. The rate of increase was slightly greater when the pieces were exposed flesh side up. This may be due in part to the greater affinity of water for the mucoid proteins in the adhering adipose tissue.

Comparative average losses in weight of disks stored flesh side up at relative humidities of 60, 76, 80, 84, 88, and 90 per cent, respectively, and 30° C. are shown in Figure IV as percentage of the initial weight of salt-cured calfskin. Each value given in Figure IV is an average obtained with two separate disks cut from the same salt-cured calfskin. The disks were prepared in the same manner as described for the previous experiments. The initial moisture and salt content of this skin were 50.4 per cent and 12.8 per cent, respectively.

As might have been expected, the rate of loss increased as the relative humidity decreased. After 8 days storage at 60 per cent relative humidity, the skin lost 20.7 per cent of its original weight as compared to a loss of 5.4 per cent at 90 per cent relative humidity. Thus, it would appear that appreciable weight losses during short time storage periods could be avoided by storing at relative humidities of 88 to 90 per cent. Also, from the standpoint of conservation during storage for long periods of time, 90 per cent relative humidity would probably be the highest constant humidity which could be considered safe for at 92 per cent, a marked uptake of moisture may occur sufficient to render salt-cured hides dripping wet.

### Discussion and Summary

These results were obtained with individual skins cured with commercial salt alone. The addition of preservatives or denaturants to salt presumably would affect the values appreciably, as would also impurities in the salt. They were also gotten with either diced samples or pieces of skin with full

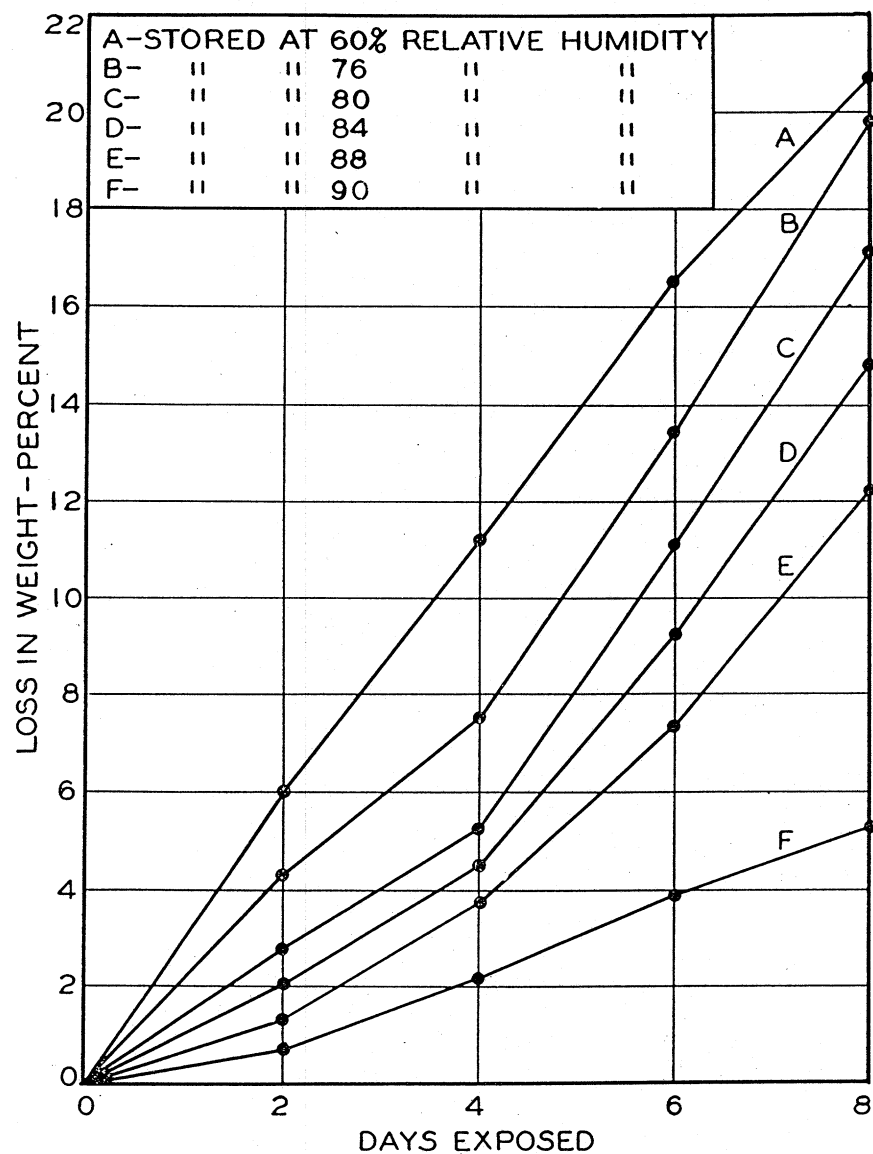


FIGURE IV. Percentage loss of initial weight by salted calfskin stored flesh side up at relative humidities of 60, 76, 80, 84, 88, and 90 per cent, respectively, and 30° C.

exposure of one surface. The values, therefore, definitely represent maximum effects as compared to bundled or piled hides and skins.

The high relative humidity found necessary to prevent weight shrinkage in the storage of salt-cured skins was rather surprising. It is believed that this level is materially higher and of a more critical nature than is appreciated generally.

The tendency for salted skins to continue to take up moisture at a high humidity constitutes a definite storage hazard from the standpoint of bacterial activity. Thus, for those cured skins with which an attempt is made to maintain weight by storing at high relative humidities, the addition of small amounts of suitable chemicals to increase the preservative action of the curing salt appears to be highly desirable.

The initial rate of loss of moisture at relative humidities of 90 per cent or less would seem to be a straight line function of time for any given humidity. Rate losses become greater as the relative humidity decreases.

High relative humidities of from 92 to 96 per cent are necessary to prevent significant losses in weight of stored salt-cured calfskins. The accurate maintenance commercially of constant weight through regulation of humidity would not appear practicable, however, since within the above narrow range in relative humidity variations of nearly 30 per cent in the moisture content of the stored skin can occur.

Davidson and Gregory<sup>4</sup> have observed that a relative humidity of 93 per cent at 30° C. was the lowest one at which hair and scutula would adsorb enough moisture to support the germination of the spores of *Dermatophytes*. This value is in close agreement with the lowest relative humidity found at which salt-cured skins will take up or hold enough moisture to support microbial activity. In these studies the dried salted skin did not take up measurable amounts of water at relative humidities lower than 86 per cent.

Innes<sup>5</sup> has shown that pure dry sodium chloride will start to take up moisture at a relative humidity just above 80 per cent. This suggests that the hygroscopic properties of the skin proteins themselves are a factor in influencing the point at which a salt-cured skin will take up or lose water to the atmosphere. A few observations were made which further suggested that an increase in the hygroscopic properties of skins might be expected as microbial deterioration progresses and is dependent possibly upon the resulting peptide fragments, since these are especially hygroscopic.